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The hygrothermal aging process and mechanism of the novolac epoxy resin

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ABSTRACT

Novolac epoxy resins, with the high glass transition temperature (T_g) and excellent mechanical strength, are widely applied in the molding and sealing compounds for the production of electronic devices. However, weather exposure and environmental elements are inclined to affect their durability severely. This work focuses on the hygrothermal aging process and mechanism of the novolac epoxy resin. The effect of humidity and time in hygrothermal aging on structural and mechanical properties of the novolac epoxy resin was deeply studied. The moisture absorption increases linearly with the square root of aging time, and it follows the Fick's second law. There are two main categories of reactions in hygrothermal aging: the first one is the post curing process, which leads to a larger crosslinking density and a reduced interior stress; while the other is the plasticization and deterioration of epoxy resin attributed to moisture ingress. The combination of above factors leads to a decrease-increase-decrease variation in mechanical properties. This work is believed to benefit the wide and safe application of a certain novolac epoxy resin system in engineering application.

1. Introduction

Resin matrix composites boast high specific strength, favorable thermal and chemical stability, strong designability, and excellent fatigue resistance, and thus they are widely used in marine, offshore and civil infrastructure applications [1–5]. Amongst them, novolac epoxy resins, with the high glass transition temperature (T_g) and excellent mechanical strength, are widely employed in the molding and sealing compounds for the production of electronic devices [6–8].

In some certain application areas, environmental factors, such as heat, moisture, ultraviolet, and varied loads, or their combinations may degrade the material properties [2,9,10]. Weather exposure and environmental elements are inclined to affect the durability of materials severely [11]. And the environmental durability of materials is one of the limiting factors for their application [12]. While compared to the fiber in composites, the resin matrix is more susceptible to elevated temperature and humidity [13]. Much work has been done to investigate the effect of aging temperature on material properties [14–18]. In this work, we will pay more attention to the influence of varied humidity on the hygrothermal aging of a new type of epoxy.

The absorption of moisture penetrating from exposed surfaces induces both reversible and irreversible changes in material constituents and properties. Reversible changes are physical variations in nature, involving both property and dimensional changes [19,20]. Some aging effects such as softening and plasticization, can be recoverable at the initial stage of hygrothermal aging when the absorbed water is eliminated and no chemical reaction occurs [21,22]. While prolonged environmental exposure leads to permanent irreversible property alterations. The different possible competitive mechanisms which establish the durability during hygrothermal are: (a) additional cross-linking due to residual curing, (b) secondary cross-linking between the polymer chains and the water molecules, (c) swelling, (d) micro-cracking, (e) leaching of low molecular weight segments (decomposition), (f) plasticization, (g) polymer relaxation, etc. [14,19,23–26].

In hygrothermal process, water uptake process changes with temperature and humidity. Both of them influenced the diffusion coefficient and equilibrium moisture absorption content [16,17,27].

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T_g can be regarded as the most useful parameter revealing material degradation [28]. A decrease in T_g is generally attributed to plasticization and deterioration, while an increase in T_g is derived from a post-curing phenomenon during hygrothermal process. Besides, Fourier transform infrared spectroscope (FT-IR), thermal gravimetric analysis (TGA), and dynamic thermomechanical analysis (DMA) can be adopted to analyze the constituent and structure changes in resin molecules during the whole process of aging [14,29–31]. Mechanical tests can be conducted to study the variation of strength and modulus [9,10,27,32–35]. In addition, scanning electronic microscopy (SEM) can help to study the micromorphology.

In this present study, a new type of cured novolac epoxy resin underwent a 28-day aging process at a constant temperature of 60 °C. To investigate the influence of humidity of hygrothermal aging, we carried out three sets of experiments, i.e., immersing a set of samples into deionized water (Case I), and placing two sets in the constant temperature humidity chamber with the relative humidity (RH) of 98% (Case II) and 65% (Case III), respectively. The duration of 0, 2 h, 6 h, 1 day, 3 days, 1 week, 2 weeks, and 4 weeks for each case were selected to study the impact of aging time. This work is expected to be helpful in understanding the effects of hygrothermal aging on the long term durability of epoxy resin in harsh service environment. It is believed to benefit the wide and safe application of a certain epoxy system.

2. Experimental procedure

2.1. Sample preparation

The novel material was a cured system of resin and rubber. Regarding the reactants, epoxy resin 618 (also called epoxy E51) and phenolic epoxy resin F-44 were purchased from Shanghai resin factory Co., Ltd., epoxy resin AFG-90, Andebao from Shanghai Huayi Resins Co., Ltd., and carboxyl-terminated butadieneacrylonitrile (CTBN) from Shenzhen Jiadida Chemical Co., Ltd. Above four materials were cured with the assistance of the curing agent, 4, 4′-diaminodiphenyl sulfone (DDS) and the accelerator, triphenyl phosphine (PPh_3), both of which were bought from Sinopharm Chemical Reagent Co., Ltd. These chemical agents were used without further purification.

The epoxy resin 618, phenolic epoxy F-44, epoxy resin AFG-90, and CTBN with the weight ratio of 9:6:4:1 as well as some certain PPh_3 were added into a 1000 mL flask and mechanically stirred at 125 °C for 48 h 100 g above resin/rubber mixture and 32.27 g DDS were blended and mechanically stirred at 170 °C for 15 min. Afterwards, they were poured into a mold with a cavity of 160 mm × 150 mm × 5 mm in a 170 °C oven for 2 h. The samples were further sectioned with a universal cutting machine (WZY-240, China) into the dimension to the requirements of following tests.

2.2. Hygrothermal aging process

The samples of Case I were immersed in deionized water at 60 °C. While the hygrothermal aging for Case II and Case II were performed in the constant temperature and humidity test machine (CZ-A-408G, Shanghai, China) at 60 °C with the relative humidity of 98% and 65% respectively. Eight kind of aging time of 0, 2 h, 6 h, 1 day, 3 days, 1 week, 2 weeks, and 4 weeks for Case I (immersed in water), Case II (RH = 98%), and Case III (RH = 65%) were carefully characterized and analyzed in this study.

2.3. Gravimetric measurement

Twelve specimens (35 mm × 35 mm × 3 mm) were applied for each case. Before hygrothermal aging, the weight of each sample W_0 was measured and recorded. At the time point of 0, 2 h, 6 h, 1 day, 3 days, 1 week, 2 weeks, and 4 weeks, in the aging process, samples were taken out of the constant temperature humidity chamber, wiped dry with tissue paper and weighed by an electronic scale with a precision of 0.01 mg. And then they were quickly put back in the chamber again for further hygrothermal aging. The average weight and the standard deviation of twelve specimens were recorded and calculated.

The moisture absorption content M_t is defined in Equation (1):

$$M_t(\%) = \frac{W_t - W_0}{W_0} \times 100 \quad (1)$$

where W_t and W_0 are the sample weights at time t and initial state, respectively.

2.4. FT-IR

The samples aged for 28 days in Case I, Case II, and Case III together with the unaged resin were analyzed on an FT-IR spectroscope (Nicolet IS10, the USA) over a wave number range of 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. The FT-IR samples were pressed together with KBr powder.

2.5. TGA

The specimens aged in three cases after 28 days and unaged resin were conducted thermo-gravimetric analysis on a Netzsch TG 209F1 (Germany) with the nitrogen purging. The samples were heated from room temperature to 900 °C, at a heating rate of 10 °C/min.

2.6. Tensile property test

In order to study the influence of the humidity and the duration time of hygrothermal aging on the tensile properties, a tensile test was performed on the Mechanical testing machine (MTS, CMT5105, the USA) with a crosshead speed of 1 mm/min. At least five specimens for each duration time and each case were conducted and recorded. Note that the sample dimension was 250 mm × 15 mm × 3 mm.

2.7. Flexural property test

The three-point bending test was carried out by the MTS CMT5105 (the USA) with a crosshead speed of 1 mm/min and the support span of 48 mm. At least five specimens for each duration time and each case were conducted and recorded. Note that the sample dimension was 60 mm × 10 mm × 3 mm.

2.8. DMA

DMA of the epoxy samples for each time and each case was performed in three-point bending mode on NETZSCH DMA 242 (Germany) at a frequency of 1.0 Hz, with a heating rate of 10 °C/min from 30 °C to 210 °C. At least three specimens for each duration time and each case were conducted and recorded. Note that the sample dimension was 50 mm × 10 mm × 3 mm.

2.9. SEM

The tensile fracture surface of specimens aged in three cases after 28 days and the unaged resin were observed on a scanning electron microscope (Tescan MAIA3 XMH, Czech). Data were